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Major Goals: The major goals of the proposed research is to explore self-assembly of organic charge-transfer crystalline materials with emerging properties. Materials-by-design and self-assembly principles are applied to organic functional materials to control their morphology, interface, and crystalline structures. The centimeter-sized charge transfer crystalline superstructures are achieved, which pave the way for the study of their intrinsic multifunctional properties, such as dielectric, magnetic, optoelectronic, and magnetoelectric coupling behaviors. The control of organic crystallization and interfacial electron coupling are keys to dictate external stimuli-responsive behaviors in organic charge-transfer superstructures. The integrated experimental and computational study reveals the importance of chemically driven interfacial coupling in organic charge-transfer superstructures. Such degree of engineering opens up a new route to develop a new generation of functional organic materials, enabling important advance in all-organic electronics.

Accomplishments: In this project, we aim at utilizing the material design and assembly strategies to rationally develop organic multiferroic-photovoltaics. Instead from trial-and-error design, we combine atomic-scale theoretical prediction and supramolecular assembly engineering to discover new stimuli-controlled multifunctional properties, in addition to the breakthroughs of optoelectronic device performance. The new multifunctional materials with air stability developed by us are critical for ubiquitous optoelectronic and multiferroic applications.

Achievement 1: World-recorded carbon photovoltaics.
Nano-carbon design and assemblies based on ab-initio predictive modeling allow us to uncover and control exciton dynamics and charge transport for developing high efficiency and robust all carbon photovoltaics, consisting of single-wall carbon nanotubes (1D), fullerenes (0D) and graphene derivatives (2D). The strategy – noncovalent self-organization – benefits from self-assembly nature inherent to all carbon (sp2) nanomaterials. This opens up new possibilities for making all-carbon assemblies without the need for any surface functionalization or dispersing agents for SWCNTs. All carbon assemblies can absorb and exchange energy through different physical mechanisms depending on the length scale. The charge and energy transfer and other attributes of interest can be related to all carbon donor and acceptor combinations, well-defined interfaces and morphologies. The molecular scale arrangement has been shown to dramatically affect the donor-acceptor charge transfer and overall optoelectronic performance.

Achievement 2: Role of supramolecular charge-transfer crystal (self-assembly) in multiferroics.
Multiferroics based on organic charge-transfer salts, exhibiting simultaneous dipolar and spin ordering, have drawn significant interests due to the prominent applications using spin-driven ferroelectricity or charge-order-driven magnetism for multiple-state memories, sensors and radio-frequency devices. In the past, merohedral

transformation induced spin ordering and the dimerization through the spin-Peierls mechanism of polar lattices leads to a broad magnetic and polarization switching temperature (Tc) range, which is in general far below room temperature. Here, we describe supramolecular co-crystallization of electron donor and acceptor for the formation of three-dimensional charge-transfer network to achieve the localized spin and charge ordering for room temperature organic multiferroics. This supramolecular motif directs the dimensional and chemical control of charge-transfer network that could switch polarization and magnetization under external stimuli, which could open up a new class of supramolecular nanoferronics.

Achievement 3: Organic van der Waals 2D heterostructure with unusual magnetoelectric and optoelectronic coupling behaviors.
Two dimensional (2D) heterostructures based on weak interlayer van der Waals (vdW) interaction with the lack of superficial dangling bonds afford multiple degrees of freedom for the creation of new high-quality 2D heterojunctions and superlattices without the constrains of lattice parameters, enabling customized and tunable optical-electrical-magnetic properties. we report a modified Langmuir-Blodgett method to assemble and organize two-dimensional (2D) molecular charge transfer crystals into arbitrarily and vertically stacked vdWHs, consisting of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)/C60 and poly(3-dodecylthiophene-2,5-diyl) (P3DDT)/C60 nanosheets. The charge transfer dependent external stimuli response, as well as broadband photoresponse suggests a strong and anisotropic interfacial coupling between the charge transfer pairs in such vdWHs. 2D charge transfer heterostructures exhibit excellent pressure dependent sensitivity with a high piezoresistance coefficient of -4.4×10-6 Pa-1, and external stimuli (ferroelectric field and magnetic field) tunable conductance and capacitance. Density Functional Theory (DFT) - based calculations confirm charge transfer between the n-orbitals of the S atoms in BEDT-TTF of the BEDT-TTF/C60 layer and the π^* orbitals of C atoms in C60 of the P3DDT/C60 layer contribute to the inter-complex charge transfer. These results are expected to stimulate the generation of a new family of 2D molecular vdWHs with tunable opto-magneto-electric coupling properties for flexible electronic applications.

Achievement 4: Self-powered organic conducting materials enabled by materials-by-design and assembly.
Self-powered organic conjugated materials are of vital importance for the development of next-generation, flexible, and fully-integrated energy, sensing, and artificial intelligence technologies. Due to their exceptionally long spin lifetimes and strong spin-charge interactions, these carbon materials could also impact data transmission, processing, and storage. However, to exploit these opportunities, the ability to directly convert energy from spin information to electric charge is essential. We introduce a novel molecular spin-charge converter that is comprised of a centimeter-sized free-standing organic charge-transfer crystal. Magnetic field effects in this material induce intersystem crossings and spin-charge-lattice couplings that generate an electric voltage for magnetic energy harvesting. The effective conversion between charge and spin stimulus permits simultaneous and instantaneous self-powering and sensing performance in a molecular crystal that displays anisotropic behavior dependent on crystal orientation. We confirm the strong charge transfer character of the crystals with first principles calculations of the electronic density of states. The solution-processed flexible devices also exhibit an excellent temperature sensitivity of < 0.01 K and a unique piezoresistance coefficient of -5.1×10-6 Pa-1. The self-powered sensing performance of this molecular spin-charge converter, together with its solution processability and flexibility, endow this molecular charge-transfer crystal with the capability to drive a new generation of non-contact magnetic energy harvesting and sensing technologies.

Training Opportunities: A number of research positions open up the opportunities to recruit and train the postdoctoral, graduate, undergraduate and high-school students. By the end of this project, two graduate students have completed their thesis work under this project, and eight undergraduate students have learned the hands-on research experience of organic material assembly for photovoltaic applications. In addition, two high-school students have their summer intern on this project and they are currently pursuing their college degree.

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Results Dissemination: Total twenty-two peer-reviewed articles are published during the reporting period.

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[15] W. Qin, X. Chen, H. Li, M. Gong, G. Yuan, J. Grossman, M. Wuttig and S. Ren*, Room temperature multiferroicity of charge transfer crystals, ACS Nano, 9, 9373 (2015)
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Honors and Awards: 2015 Temple University - “Rising Star”
2015 NSF - CAREER
2015 RSC Emerging Young Investigator - J. Mater. Chem.

Protocol Activity Status:

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Technology Transfer: My group has been actively collaborating with the ARL material scientists, including Dr. Raymond Brennan on high-frequency dielectric and magnetic measurements of self-assembled organic crystals, and Dr. Victoria Blair on high-temperature XRD and synchrotron studies of materials. Three joint publications have resulted from this collaboration in this reporting period.

PARTICIPANTS:

Participant Type: PD/PI
Participant: Shenqiang Ren
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Wei Qin
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Beibei Xu
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Maogang Gong
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Zhuolei Zhang
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Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

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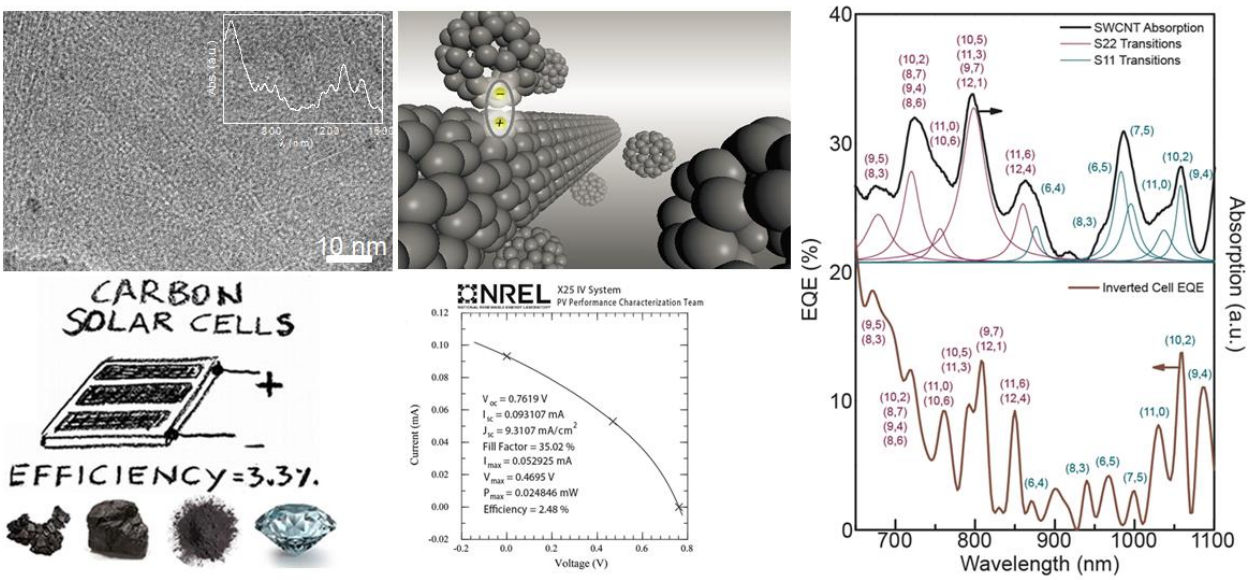

Fig.1. The TEM and schematic image of carbon donor-acceptor assembly (top left); The world-record power conversion efficiency in carbon nanotube based photovoltaics, certification by NREL (bottom left); The chirality-dependent external quantum efficiency (right).

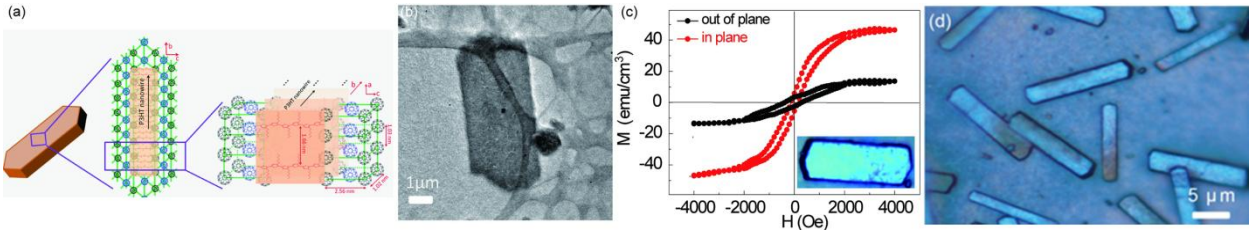

Fig. 2. (a) Schematic images of supramolecular assembly processing of organic charge-transfer complexes, consisting of thiophene electron donor and C_{60} acceptor. (b) TEM image of nanoribbon-like organic charge-transfer crystals. (c) Magnetic hysteresis loop of organic charge-transfer complex exhibits magnetic anisotropy due to the crystal growth. The inset shows the optical microscopy image of charge-transfer crystals after supramolecular processing. (d) Optical microscopy image of charge-transfer crystals.